"The Effects of Heat and of Solvents on Thin Films of Metal."
By G. T. Beilby. Communicated by F. H. Neville, F.R.S.
Received June 4,—Read June 18, 1903.

[Plates 11—13.]

In the Bakerian Lecture of 1857,* on "Experimental Relations of Gold and other Metals to Light," Faraday described a series of experiments which were designed to throw light on the structure and behaviour of metals in their most attenuated forms. Probably the most remarkable of these experiments were those in which leaves and films of gold and silver supported on glass were changed by a temperature much below the melting point of the metal from a moderate translucence to clear transparence and from high metallic reflecting power to comparative deadness.

These remarkable experiments seem practically to have dropped out of sight during the past 45 years for, so far, I have found no reference to this particular phenomenon in the papers of more recent workers on the reflecting and absorbing powers of thin metal films, and many physicists to whom I have shown these Faraday films have received them as a novelty.

The significance and explanation of the change produced by heat is discussed by Faraday at several stages of the lecture. Two alternative explanations are suggested by him. Under the first, it is supposed that the heating may act by gathering the metal into small aggregates, thus leaving the surface like a grating through which light can freely pass. Under the second, the leaf or film is supposed to be made up of scale-like films, the effect of heating being to open these up like the louvres of a blind, thereby allowing the light to pass freely between them. A third suggestion may be read into some of Faraday's remarks, namely, that metal in the non-reflecting transparent condition is an allotropic modification of the common or reflecting form.

While studying the appearance and structure of surface films on metals in their more massive forms,† it occurred to me that considerable light might be thrown on that subject by a parallel study of the behaviour of translucent films supported on glass, as these present the great advantage for microscopical examination that they permit of the use of transmitted light.

The result of this parallel study has been to show that both aggregation and film formation come into play when metal leaves and films are heated, but that an intrinsic transparence exists altogether apart from these phenomena.

* 'Phil. Trans.,' 1857, p. 145.
† 'British Association Report,' 1901, p. 604.

As a further result of this study, it is now suggested that the behaviour of surface films during heating may be most satisfactorily explained on the hypothesis that even at a temperature much below the melting point, sufficient freedom is conferred on the molecules by the heating to enable them to behave as the molecules of the liquid metal would do, and to arrange themselves under the influence of surface tension either in films or in drop-like or granular forms.

Faraday definitely associated diminished transparence and enhanced reflecting power with a state of strain induced by pressure and burnishing. My later observations confirm and extend this conclusion and show that, contrary to my first impression, all mechanical disturbance of the surface by polishing or burnishing tends to diminish transparence and to increase the reflecting power.

In gold an olive green colour by transmitted light is generally associated with the strained condition, while a great variety of shades of colour, ranging from ruby-red to violet, are found in the annealed metal.

A gold leaf, after annealing on glass, retains all the ribs and markings of the original leaf. These interfere with the uniform adhesion between the metal and the glass, and lead to obvious breaks in continuity. Fig. 13 (Plate 11) shows a piece of gold leaf annealed on glass. Small granular aggregations are seen, but the continuity of the film between these is not so obvious.

Faraday describes how he prepared gold films of varying thickness and of great smoothness and continuity by placing specks of phosphorus on the surface of a dilute solution of gold chloride.

Films made in this way were annealed by heating on glass. Figs. 15 to 18 show the effects of annealing on films of various degrees of thickness.

Before annealing, the thicker films (figs. 15, 16, 17) were olive green by transmitted light and had a full yellow colour and metallic reflection by reflected light. The thickest film, fig. 15, required a very intense light to show its green translucence. Fig. 16 had the same depth of colour as gold leaf, and fig. 17 was thinner and paler. Fig. 18 was much thinner than any of the others, showed hardly any metallic reflection and its colour was blue-purple by transmitted light.

After annealing the colour of this film was rose-pink by transmitted light. The photograph shows that it was quite continuous, but with thickenings or aggregations distributed regularly over the surface. The photograph has been made somewhat dark in order that the structure may be shown more distinctly, but as seen under the microscope the surface was entirely free from dark or opaque patches.

In fig. 17 the retraction into globular or rounded forms of greater opacity is very pronounced, but the continuous transparent film

covering the whole surface is distinctly seen. Under the microscope this film was of a very pale pink colour, the thicker parts being of a slightly deeper shade. The opaque-looking granules of the photograph were really of a dark brown-green colour.

In figs. 16 and 15 the thickened patches are of larger size and of greater opacity. The transparent parts seemed as if covered with an irregular film of pink jelly dotted over with little rounded heaps.

The bright gold and platinum paints made for ceramic gilding by the Gold und Silber Scheide Anstalt of Frankfurt, supply an excellent means of obtaining continuous films of almost any thickness. In these paints the metal has been brought into perfect solution in an essential oil. A plate of glass or of mica is smoothly coated with the paint, which is allowed to dry naturally. It is then heated in an air bath to about 400°, when the solvent oil and other volatile constituents are driven off and a smooth bright metallic film is found firmly adhering to the glass. At this stage the film is translucent and green by transmitted light. If the film is kept at a higher temperature for some time it becomes more transparent, and the colour by transmitted light changes to blue or purple. By long continued heating the film assumes a frosted appearance by reflected light, and the colour becomes paler by transmitted light.

These films are sometimes blistered by air bubbles, and an excellent idea of their continuity and transparence is obtained by carefully examining the spot where a bubble has been formed. So horn-like and translucent are these films that it was at first assumed that the paint contained a binding flux or frit, but, on careful inquiry I was assured by Dr. Fritz Roessler, the scientific director of the Frankfurt Works, that the films left on the glass are pure gold and platinum and free from any flux or frit. Fig. 14 is a gold film of this kind which has been annealed to the purple stage.

The thickness of a similar film was estimated by weighing the gold from a given area. Assuming that the density of the gold in this form is normal, the thickness was 166 $\mu\mu$, or about twice the thickness of a gold leaf. Under the microscope the thickness, as seen at bubbles and broken edges, seemed to be much greater than this.

The phenomena of annealing are equally well seen in silver leaf and in films of silver chemically deposited on glass. In the case of silver, annealing takes place at the comparatively low temperature of 300° to 350°.

When the films are very thin the granular aggregations are not visible by transmitted light. As the thickness increases, the aggregations increase in distinctness, and are seen to be brown by transmitted light. The very feeble metallic reflection of these brown granules is noteworthy.

Tests of the electrical conductivity of films of gold and silver, before and after annealing, have been made for me at the National Physical Laboratory, the following is quoted from the report of th Director :—

"The tests were made on three kinds of films, viz. :—

"(A) Silver leaf on glass or mica.

"(B) Chemically deposited silver on glass.

"(C) Gold on glass or mica (applied in oil and reduced by heat).

"The general result of heating these films to temperatures above 300° C. was ultimately to increase their resistance from relatively small values (of the order of 0·2 to 50 ohms) up to very high values (thousands of megohms).

"It was also noticed, in the case of the chemically deposited silver, that the first heating seemed to produce a considerable fall of resistance (*e.g.*, from 14 ohms down to 2 ohms). Part of this change may have been due to the possibility of making better contacts after the heating.

"The following description of the specimens sent herewith will illustrate this general result.

"(A) Silver Leaf.

No.	Description.	Treatment.	Resistance.
	Specimens on glass	Not heated	0·16 ohm.
2	On glass (7·5 cm. × 3·5 cm.)	Heated about 1 hour 300° C.	0·9 ,,
8	,, ,,	Further heating above 300° C.	Over 1,000,000 megohms.
9	On mica	Further heating above 300° C.	Over 1,000,000 megohms.

"(B) Chemically deposited Silver.

18	On glass (7·5 cm. × 2·5 cm.)	Not heated	15 ohms.
15	,, ,,	Heated to 300° C. ..	2·1 ,,
14	,, ,,	Heated higher.....	Over 1,000,000 megohms.
14	,, ,,	Before heating	11 ohms.
16	,, ,,	One end more highly heated than the rest	End over 1,000,000 megohms, remainder 8 ohms.

"(C) Gold.

13	On glass (4 cm. × 1·1 cm.) ..	Heated to complete reduction	6 ohms.
17	,, ,,	Heated above 400° C.	Over 1,000,000 megohms.
11 and 12	On mica	Ditto	Over 1,000,000 megohms."

"Calculating from the ordinary conductivity of silver, a film 7 cm. long × 3·5 cm. broad, having a resistance of 3 ohms, would have a thickness of 0·00001 mm. (100 $\mu\mu$)."

Fig. 14 is a photograph of the actual film, No. 11, of the foregoing report.

Figs. 29 and 30 are photographs of the silver film, No. 14 (Bushy), by transmitted and by oblique light. The vertical band on these figures is the result of a needle scratch, which has uncovered the glass.

Neither in the case of the chemically deposited silver, nor in that of the gold paint, was there anything to suggest such complete discontinuity as the electrical tests would lead one to expect. In the gold film, especially, there appeared to be such a depth of granules in the film as would, even with the most open packing, supply a conductor of fair average cross-section. The under side of the film, examined through the glass or mica, appeared continuous, and closely adherent to its support.

Further experiments on electrical conductivity of annealed metals are now in progress.

Dr. Glazebrook has directed my attention to papers by A. C. Longden* on "Electrical Resistance of Thin Films, deposited by Kathode Discharge." According to Mr. Longden, it was found that thin films had a negative, while thick films had a positive temperature coefficient.

These conclusions obviously do not apply to annealing temperatures used in my experiments, the increase of resistance in the Bushy tests being of an altogether different order from that referred to by Mr. Longden.

When a gold leaf laid on glass by Faraday's method is exposed for a very short time to mercury vapour, minute globules of mercury condense on the surface and, amalgamating with the gold, form transparent spots. This transparence quickly spreads and the whole leaf becomes almost as transparent and free from metallic reflection as if it had been annealed by heat. When the operation is watched with the microscope the mercury is seen shooting in thin streams between the plies and folds of the gold leaf. The final effect is similar to that obtained by heat annealing; there is the same transparent granulated film covering the glass, while the thicker brown-green aggregations form a skeleton outline of the ribs and markings of the leaf. Fig. 28 is a photograph near the edge of the leaf. Outside the edge and on the right is the uncovered glass surface with globules of mercury dotted over it.

If the mercury-treated leaf is heated sufficiently to drive off the mercury a very transparent film of annealed gold is left behind.

* 'Physical Review,' pp. 40 and 84 (11), 1900, and p. 355, Dec., 1902.

In the first part of this paper it was shown that when the surface of metals is subjected to various forms of mechanical treatment a distinct covering film or layer is produced, which is in many respects different from the mass of metal below. By the regulated action of solvents this covering film can be wholly or partially removed. The observations now to be described show that the behaviour of this covering film under the action of heat annealing is in many respects analogous to that of thin films supported on glass.

For the study of these surface effects plates of pure gold were used. These were planished by beating on a polished surface, and polished by rubbing them lightly on rouged leather. The difficulty of obtaining a scratchless, untorn surface in a soft metal like pure gold is very great, but, fortunately for the purpose in view, a perfect surface was not needed, indeed the presence of lines of flow was sometimes an advantage.

Fig. 19 shows the surface of the polished plate. This and the three following figures are direct photographs without enlargement, by normally reflected light, with a 3 mm. oil immersion apochromat of 1·4 N.A. the magnification is × 1500.

Fig. 20 is the same plate after heating to between 700° and 800° for 10 minutes. The surface film has become detached and broken up, evidently by the escape of air which had been imprisoned during the planishing and polishing operations. The surface has a viscous appearance and the holes made by the escaping gas add to this effect.

Fig. 21 is the same plate after further heating for an hour. The surface film appears to be aggregating and subsiding into the mass of metal below.

Fig. 22 is the same after further heating for an hour. In this case, as exactly the same spot has been photographed as in the preceding figure, it is possible to trace the further subsidence and disappearance of the original surface film.

Fig. 23 is another specimen of polished gold after heating for 1 hour. The ruffled surface again shows the effects of escaping gas.

In Fig. 24, after a further hour's heating, the final subsidence and the viscous flow of the surface are clearly seen.

To complete the parallelism between the behaviour of thin films on glass and surface films on massive metal, a plate of polished gold was exposed for a short time to the action of mercury, which was then driven off by heat.

The exact nature of the change brought about by this treatment was at first both puzzling and obscure. The greatly increased absorption of light by the altered surface could not be accounted for on the mere supposition that it was a scattering effect due to the breaking-up of the surface, because there was evidently loss of light

not merely in one but in all directions. This loss pointed to increased absorption, and the first idea was that the escaping vapour had blown the molten alloy into multitudes of films so thin as to be devoid of reflecting power. But this view was not borne out by the behaviour under mercury treatment of films supported on glass. In their case it was found that the metal left, after the mercury had been driven off, had arranged itself in transparent granular forms of greatly diminished reflecting power (fig. 28). The loss of light then is mainly due to absorption by the more transparent metal, not to scattering by repeated reflection from films.

A knowledge of this fact is of value in interpreting the appearances presented by surfaces of gold etched by aqua regia or by chlorine. In this case also there is an immense loss of light, which cannot be caused by scattering reflection, and can only be due to increased absorption.

Fig. 25 is a spot on a gold plate which has been amalgamated with mercury and then heated. On the light part of the surface the mercury has acted very slightly, and the lustre of the original surface is not much diminished, though there has been sufficient action to bring about aggregation in rounded forms. On the dark part the action has gone deeper, and in consequence the amount of light which has escaped absorption has been insufficient to disclose the details of structure.

Figs. 26 and 27 are photographs of the light and dark parts at a higher magnification by the 3 mm. objective. In Fig. 27 the spots of light on the dark back ground are reflections from the tops of transparent or translucent granules of rounded form.

The foregoing observations on the effects of heat on thin films and on surface films show conclusively that considerable molecular rearrangement is brought about at a temperature very much below the melting point of the metal. The mere fact of there being a certain amount of freedom imparted to the molecules by heat is not surprising, in view of the well-established facts of segregation and crystal growth in masses of metal at temperatures much below their melting point. But that this freedom takes place under conditions which lead the solid molecules to behave like liquid molecules is both new and suggestive.

The appearance of viscous flow and the forms assumed by the surface film suggest neither segregation **nor** crystal growth, but they do strongly suggest the behaviour of a viscous fluid under the control of surface tension. It appears probable, therefore, that at the surface of a solid the crystallic force is controlled and kept in check, sometimes actually overpowered, by surface tension, although in the body of the metal the equally balanced molecular attractions do not effectually oppose the crystallic.

If the foregoing views are correct, it will follow that a freely suspended aggregate of solid molecules will take the spherical form if its surface is sufficiently large compared with its mass. A globule will only take the external form of a crystal when its mass becomes large enough to permit the crystallic force to overpower surface tension. The researches of Neville and Heycock* have shown that, even in the solid state, the larger crystals grow at the expense of the smaller and eventually swallow them up. The range of the crystallic force therefore widens as the mass of the crystal is increased, while the range of the molecular forces remains constant. It seems possible, therefore, that the average size of the granules in solids may result from the establishment of a state of equilibrium between these rival forces.

The bearing of these views on the theory of the formation of globular precipitates and the sphero-crystals described by Quincke† is obvious. The oily drops of calcium carbonate, which are seen as a first stage in the development of crystals, are not necessarily a super-saturated solution of calcium carbonate, they may be aggregates of solid molecules under the control of surface tension.

Mr. F. H. Neville has directed my attention to Faraday's observations‡ on the fluidity of minute globules of sulphur at the ordinary temperature. These observations seem to support the views I have advanced here.

Metals slowly deposited from solution tend to aggregate in the granular form. If the deposition takes place on nuclei floating in the solution or resting on the submerged surfaces, spheroidal granules are produced. If the deposition takes place on a clean smooth surface a thin flat film is produced, but even then the deposit is made up of flattened granules or "spicules" as I have called them in a former paper. When the thin film is annealed by heating, the flattened granules are drawn up into more distinctly rounded forms.

The flattened granule or "spicule" can be detected by oblique illumination even when it is too thin to show by transmitted light. By comparing its size and appearance under different forms of illumination when it is sufficiently massive to show by transmitted light, we are enabled to feel some confidence in the reality of those appearances which can only be seen by oblique illumination.

In the separation of solids directly from the gaseous state, *e.g.*, lamp black or magnesium oxide, the granular form is assumed by the molecular aggregates.

The more detailed study of these granular and spicular appearances will be dealt with in a further communication.

* 'Roy. Soc. Proc.,' vol. 69, p. 325.

† 'Ann. d. Physik,' vol. 7, pp. 631—682, 1902.

‡ 'Quarterly J. of Science,' vol. 21, p. 392.

DESCRIPTION OF PLATES 11—13.

(The numeration of the figures is continued from those in foregoing paper.)

PLATE 11.

Fig. 13.—Gold leaf annealed by heating on glass.
Transmitted light with green screen.
Objective 12 mm. Apo. N.A. 0·65.
Magnification × 440.

Fig. 14.—Gold paint on glass annealed by heating.
Light and objective as in fig. 13.
Magnification × 440.

Figs. 15 to 18.—Gold film, phosphorus—reduced—annealed by heating on glass.
Transmitted light with green screen.
Objective 12 mm. Apo. N.A. 0·65.

Fig. 15.—The thickest part of the film. Fig. 16.—A thinner part.

Fig. 17.—A still thinner part. Fig. 18.—The thinnest part. The dark patches were deep green, and the light patches pale pink by transmitted light.

PLATE 12.

Fig. 19.—Gold plate planished and polished.
Normally reflected light, green screen.
Objective 3 mm. Oil immersion. Apo. N.A. 1·4.
Magnification × 1500.

Fig. 20.—The same after heating for 10 minutes to 700°—800°.
Surface broken up into films by escaping gas.

Fig. 21.—The same after further heating for 1 hour.
Surface subsiding after escape of gas.

Fig. 22.—The same, after further heating for 2 hours.
Surface further subsided.

Fig. 23.—Gold plate, another specimen, heated for 1 hour.
Surface subsiding after escape of gas.
Lighting and objective as in figs. 19—22.
Magnification × 1500 (enlarged from 775).

Fig. 24.—The same after further heating for 1 hour.
The surface has subsided and has assumed an appearance of viscous flow.

PLATE 13.

Fig. 25.—Gold plate. A spot amalgamated with mercury, which was then driven off by a gentle heat. The dark part was most affected by the treatment, and the light part least.
Normally reflected light, green screen.
Objective 12 mm. Apo. N.A. 0·65. Magnification × 250.

Fig. 26.—The light part of the same more highly magnified.
Objective 3 mm. Oil immersion. Apo. N.A. 1·4.
Magnification × 775.

Fig. 27.—The dark part of the same more highly magnified.
Objective as in fig. 26. Magnification × 775.

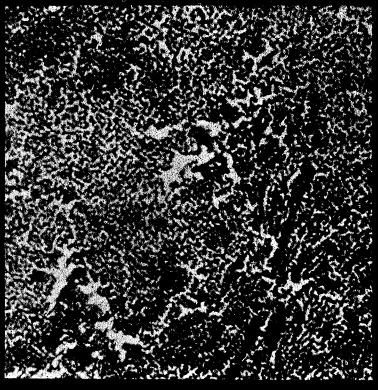


Fig. 13. X 440.

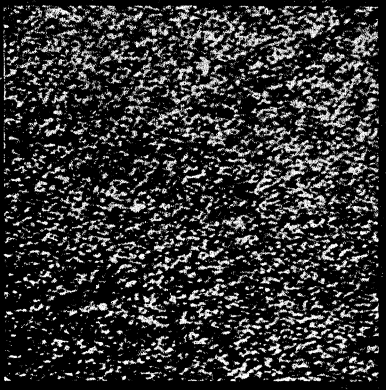


Fig. 14. X 500.

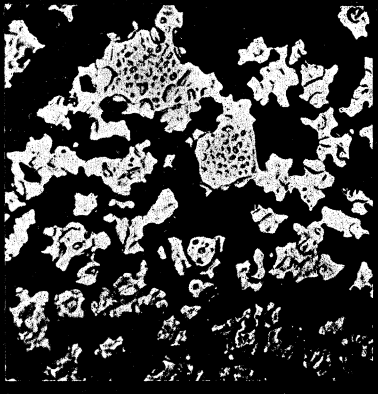


Fig. 15 X440.

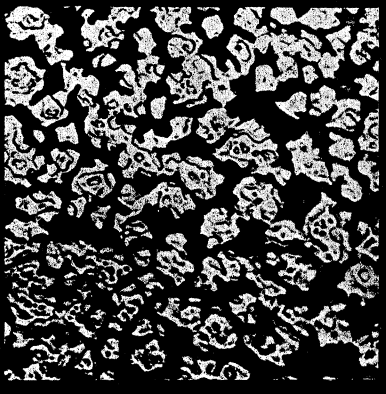


Fig. 16. X440.

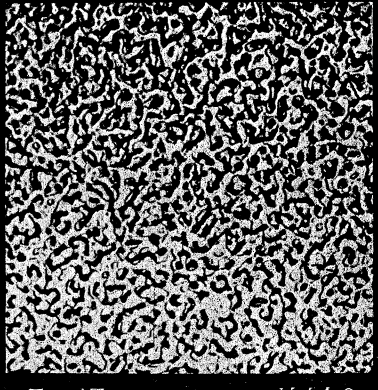


Fig. 17. X440.

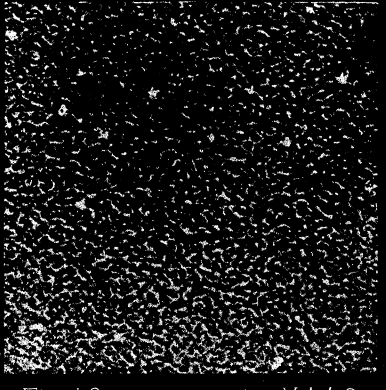


Fig. 18. X440.

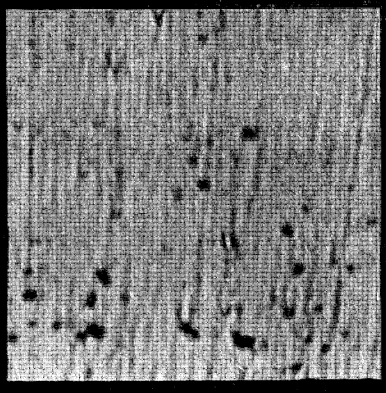


Fig. 19. X1500

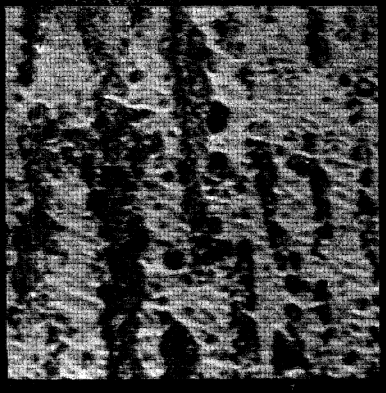


Fig. 20 X1500

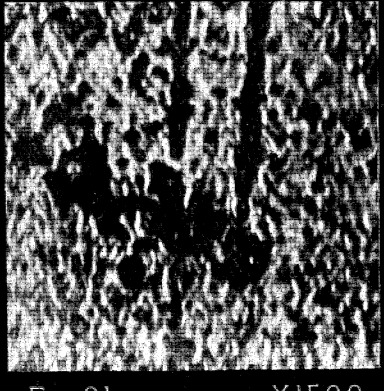


Fig. 21. X1500

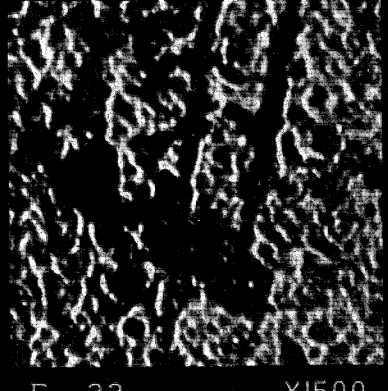


Fig. 22 X1500.

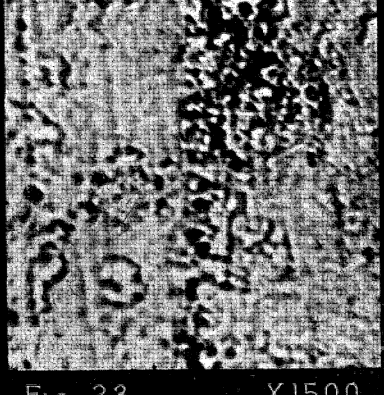


Fig. 23. X1500.

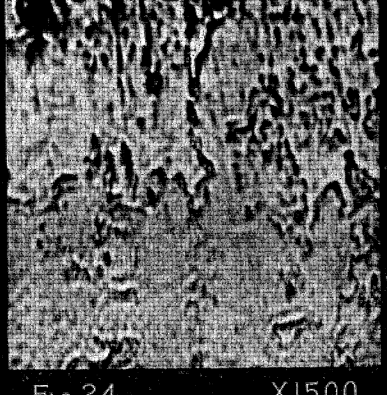


Fig. 24. X1500.

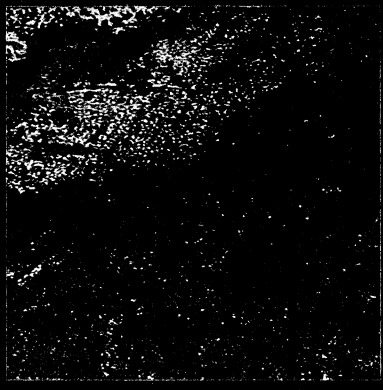


FIG 25. X 250.

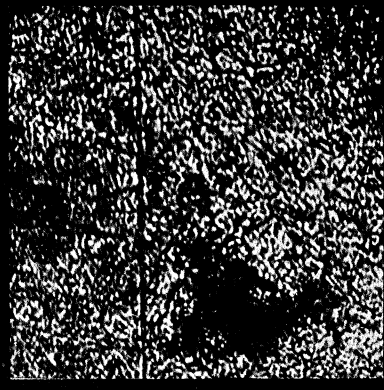


FIG. 26. X 775.

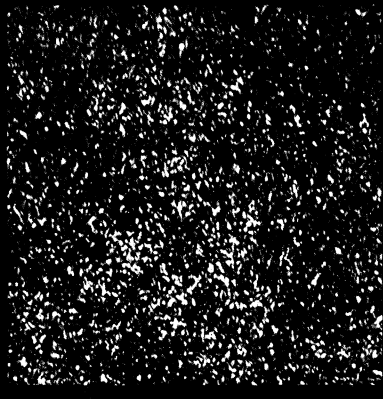


FIG. 27. X 775.

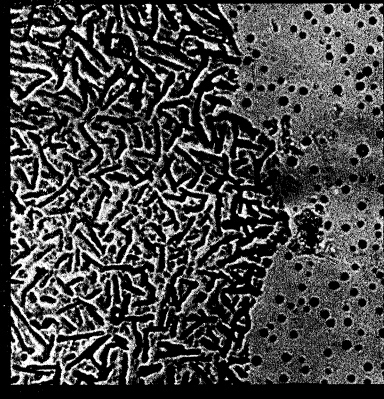


FIG 28. X 440.

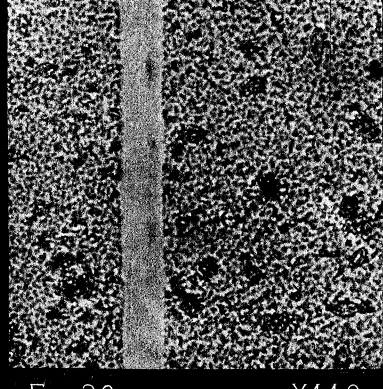


FIG 29. X440

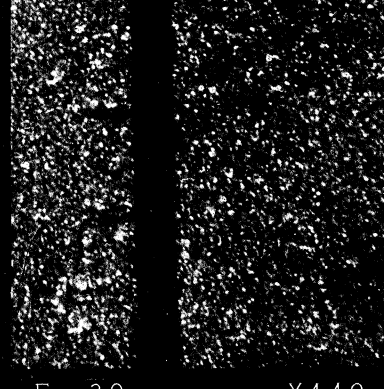


FIG. 30. X 440.

Fig. 28.—Gold leaf on glass, exposed to mercury vapour, and then heated sufficiently to drive off the mercury.
Transmitted light, green screen.
Objective 12 mm. N.A. 0·65. Magnification × 440.
The dark patches were deep green, and the clear parts between them were colourless.

Fig. 29.—Silver film on glass, annealed by heating at 350°.
Transmitted light with green screen.
Objective 12 mm. N.A. 0·65. Magnification × 440.

Fig. 30.—The same by dark ground illumination.
(Oblique transmitted light).
Objective 16 mm. N.A. 0·3. Magnification × 440.

"The 'Hunting' of Alternating-Current Machines."

By BERTRAM HOPKINSON, M.A.

Communicated by Professor J. A. EWING, F.R.S. Received June 16,—Read June 18, 1903.

Many years ago the late Dr. John Hopkinson showed that if a pair of alternating-current dynamos, A and B, mechanically separate but connected electrically in parallel, be running steadily on a constant load and with a constant driving power, and if the steady motion be slightly disturbed, say by momentarily retarding A, then A will do less and B more than its share of the work, with the result that there will be a balance of force tending to accelerate A and to retard B and so to restore the state of steady motion. In other words the two machines tend to keep in step. Similar considerations apply to a synchronous alternating-current motor worked from supply mains—it tends to keep in step with the generators supplying it.

It has been found in practice that as a general rule the paralleled alternators do keep in step, but in a not inconsiderable number of cases great trouble has been caused by a tendency in the machines to develop gradually increasing oscillations about the state of steady motion in which they are in step with one another. This oscillation or "hunting" leads to violent cross magnetising currents, and sometimes the machines drop out of step altogether. This phenomenon has received a great deal of attention from the practical side, the object being of course to put an end to it. This experimental study has resulted in empirical rules as to fly-wheel effect, and in the various damping devices or "Amortisseurs" which are now largely used on alternating-current machinery and generally give satisfactory parallel running.

Theoretical treatment of hunting has been confined (so far as I am

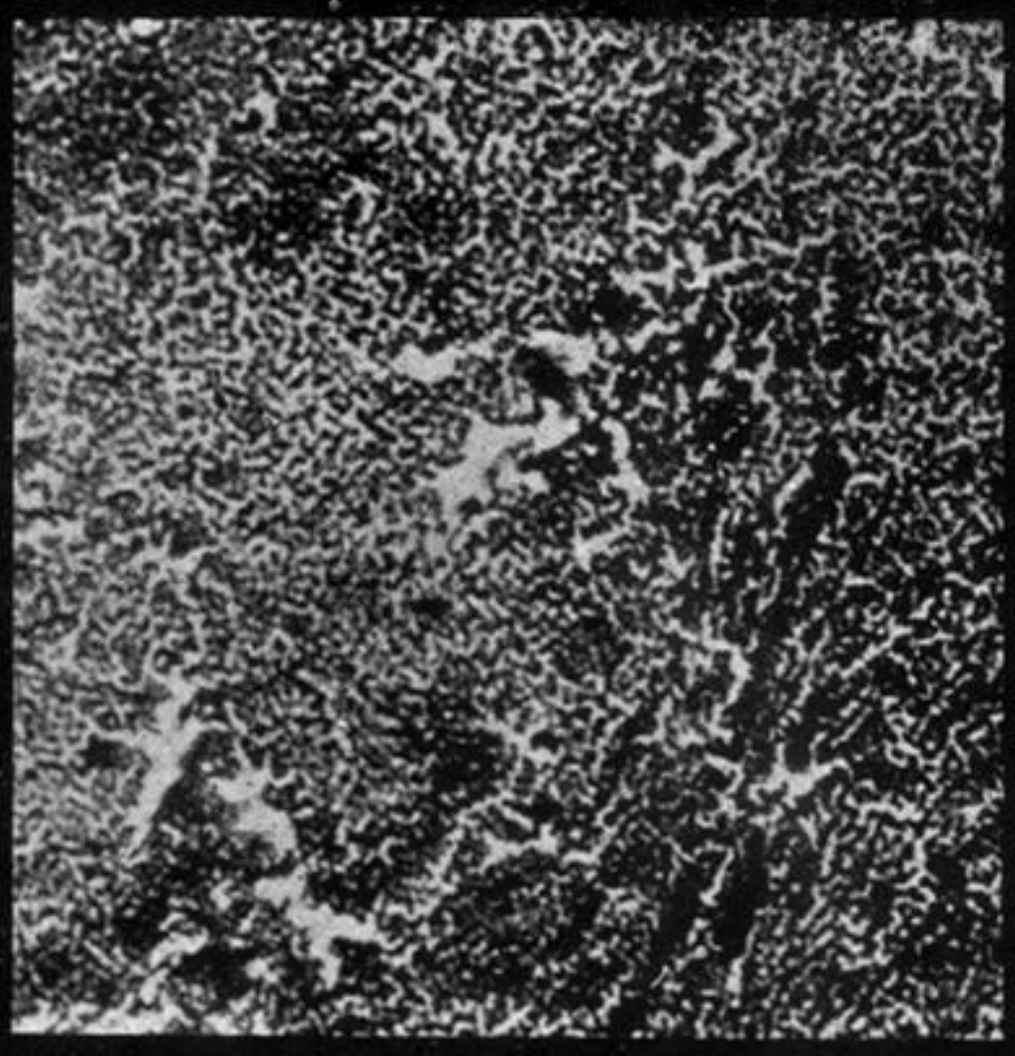


Fig. 13. X 440.

Fig. 14. X 500.

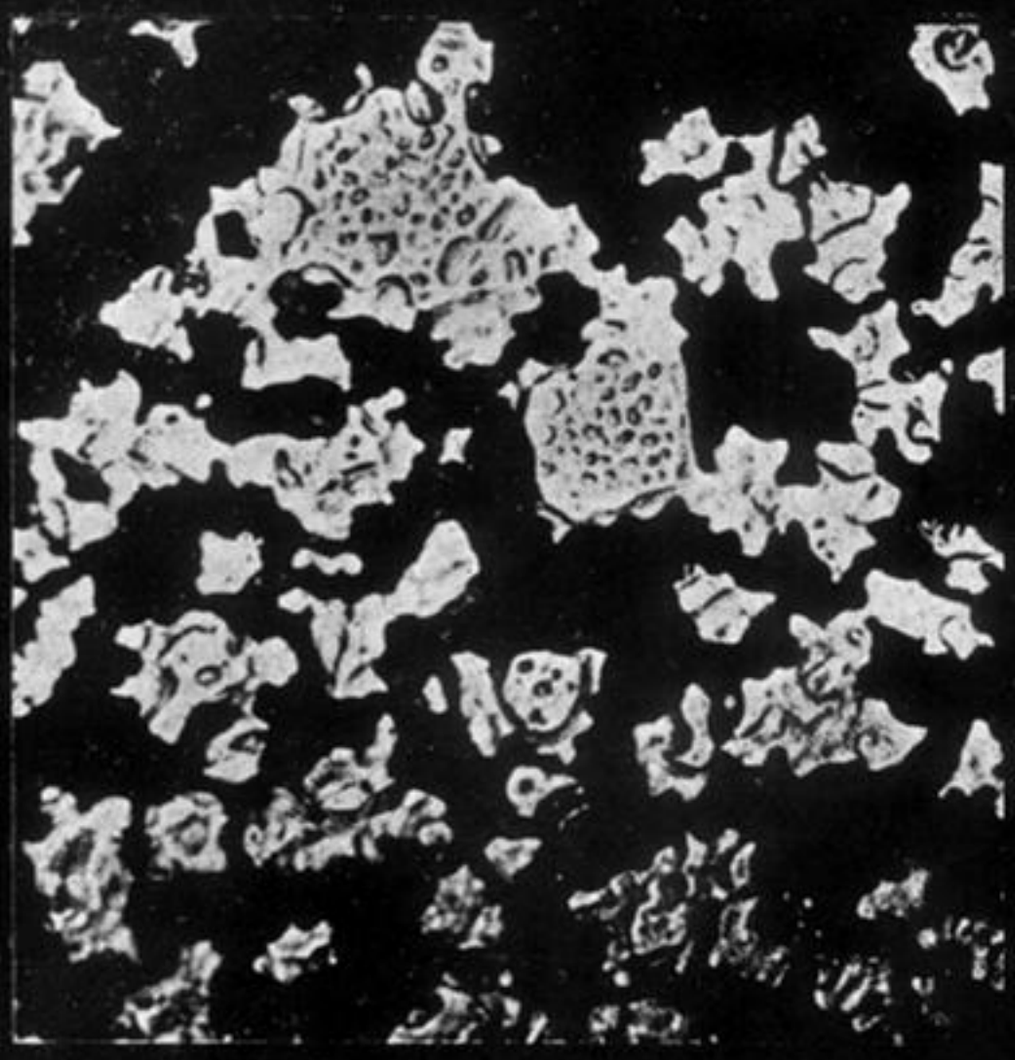


Fig. 15 X 440.

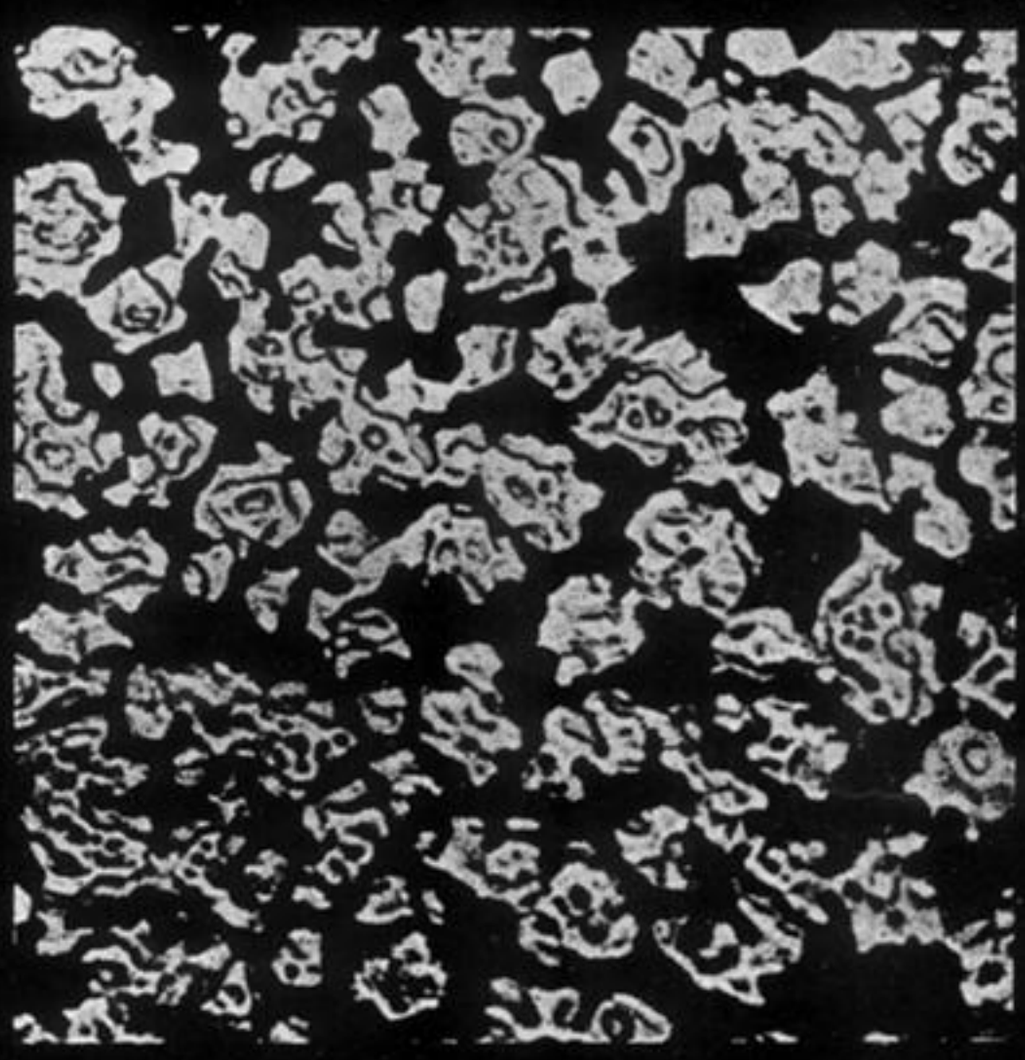
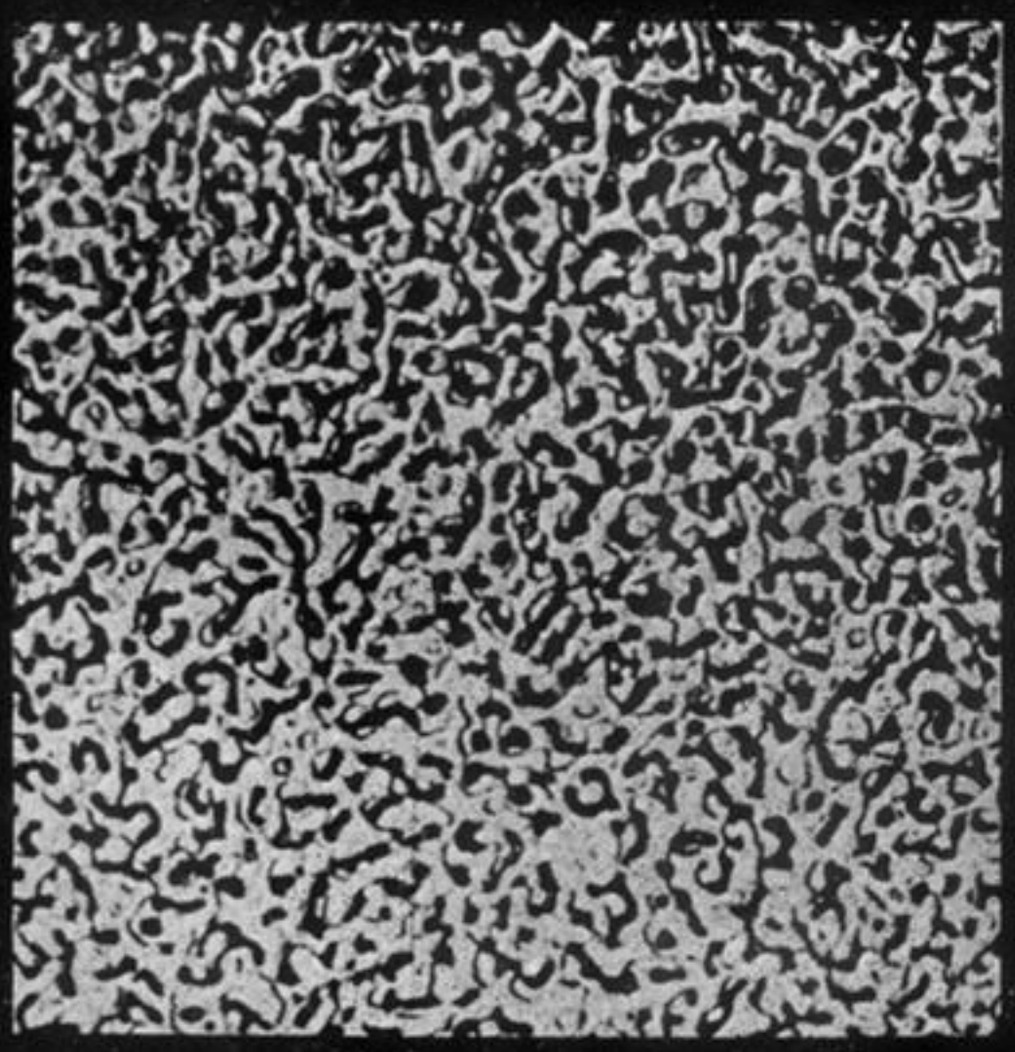


Fig. 16. X 440.



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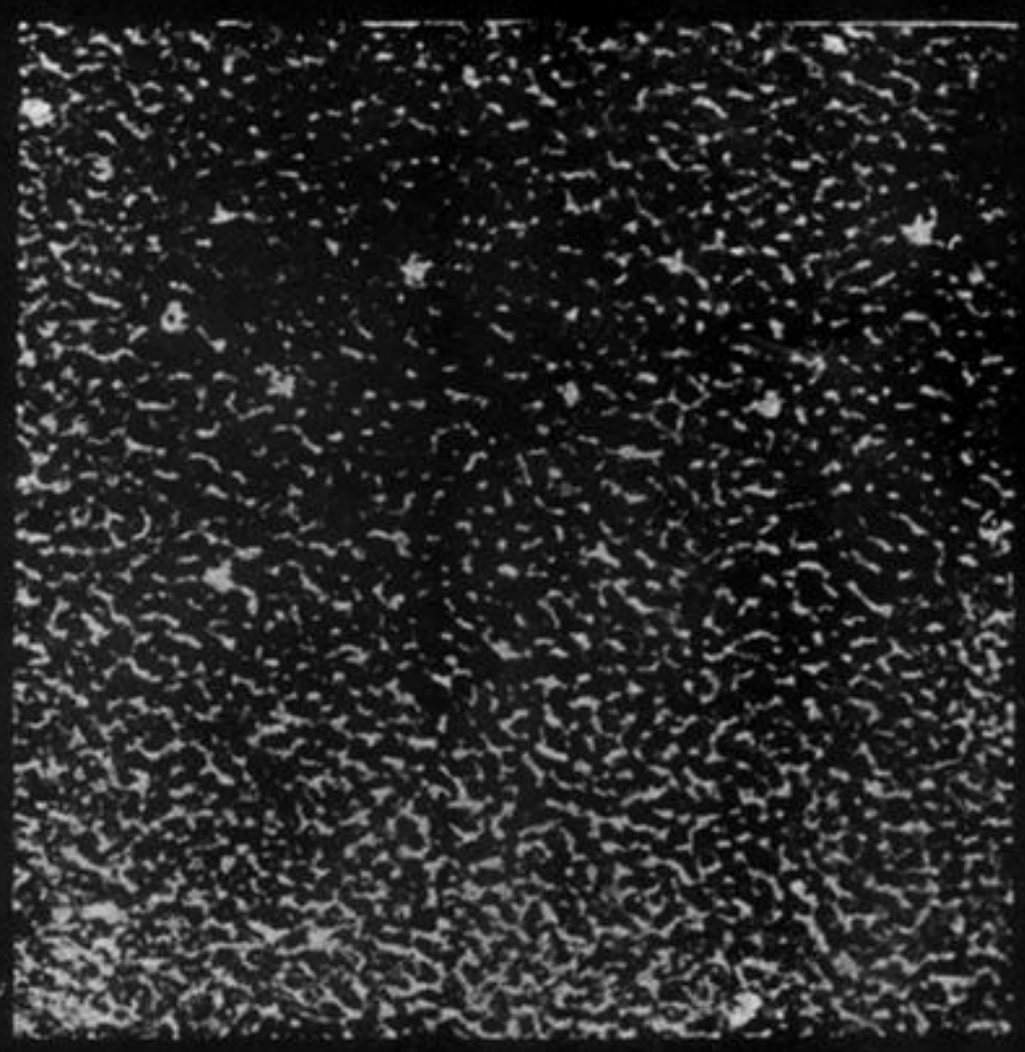

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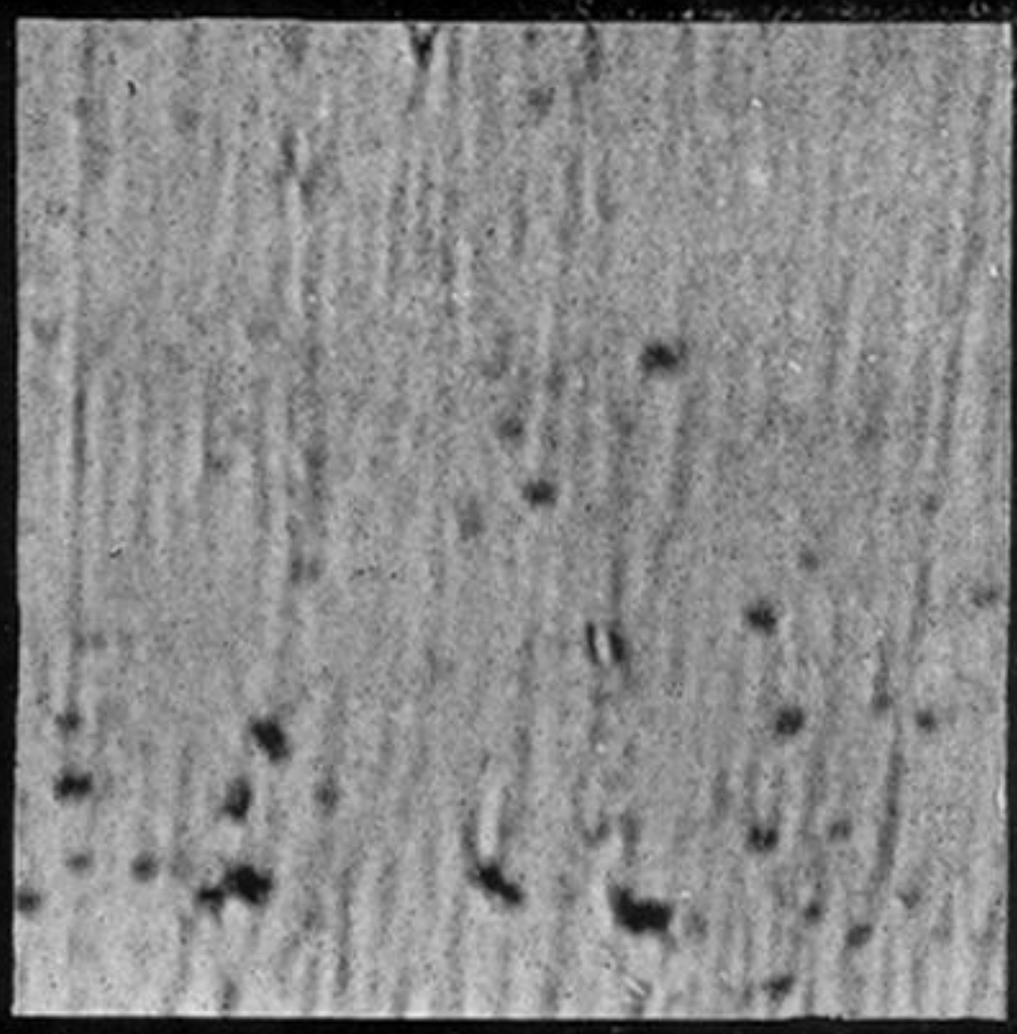

Fig. 19. X1500

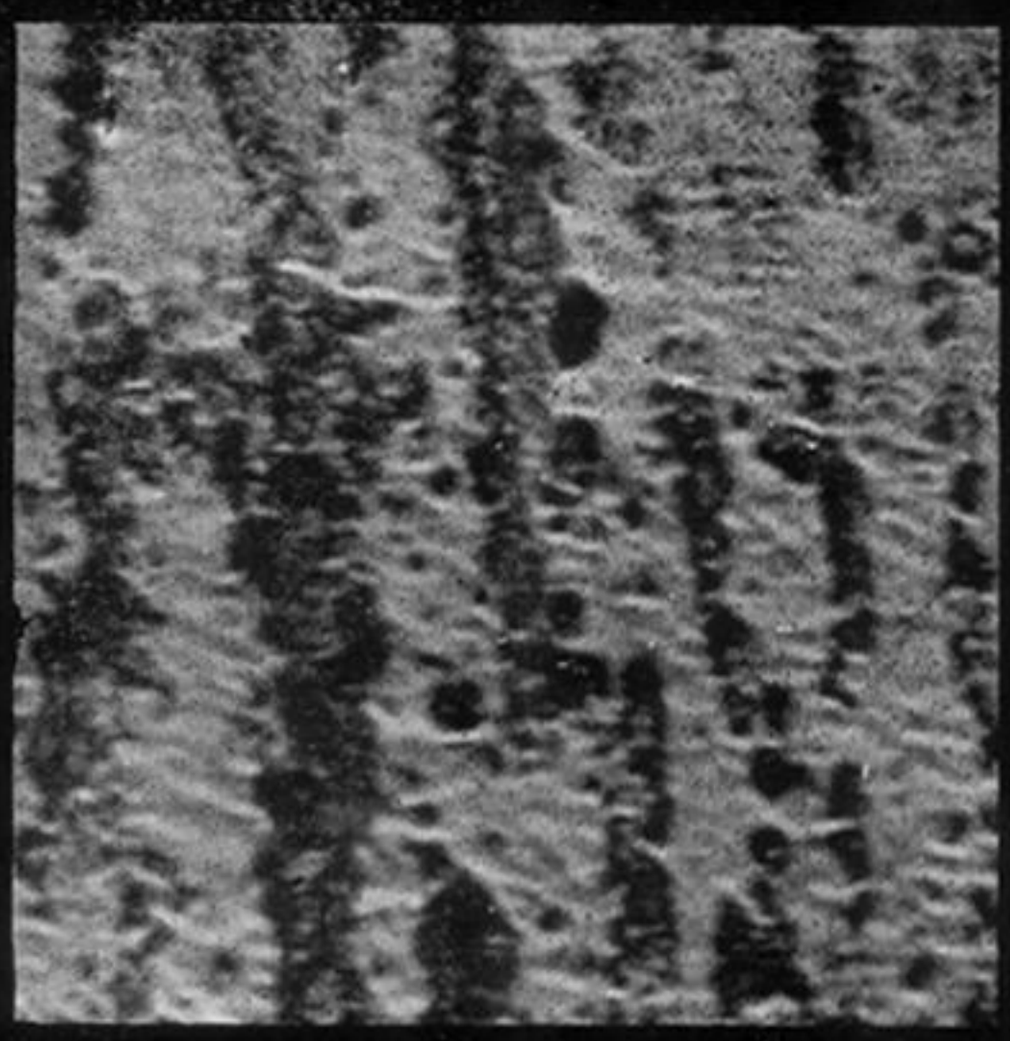

Fig 20 X1500

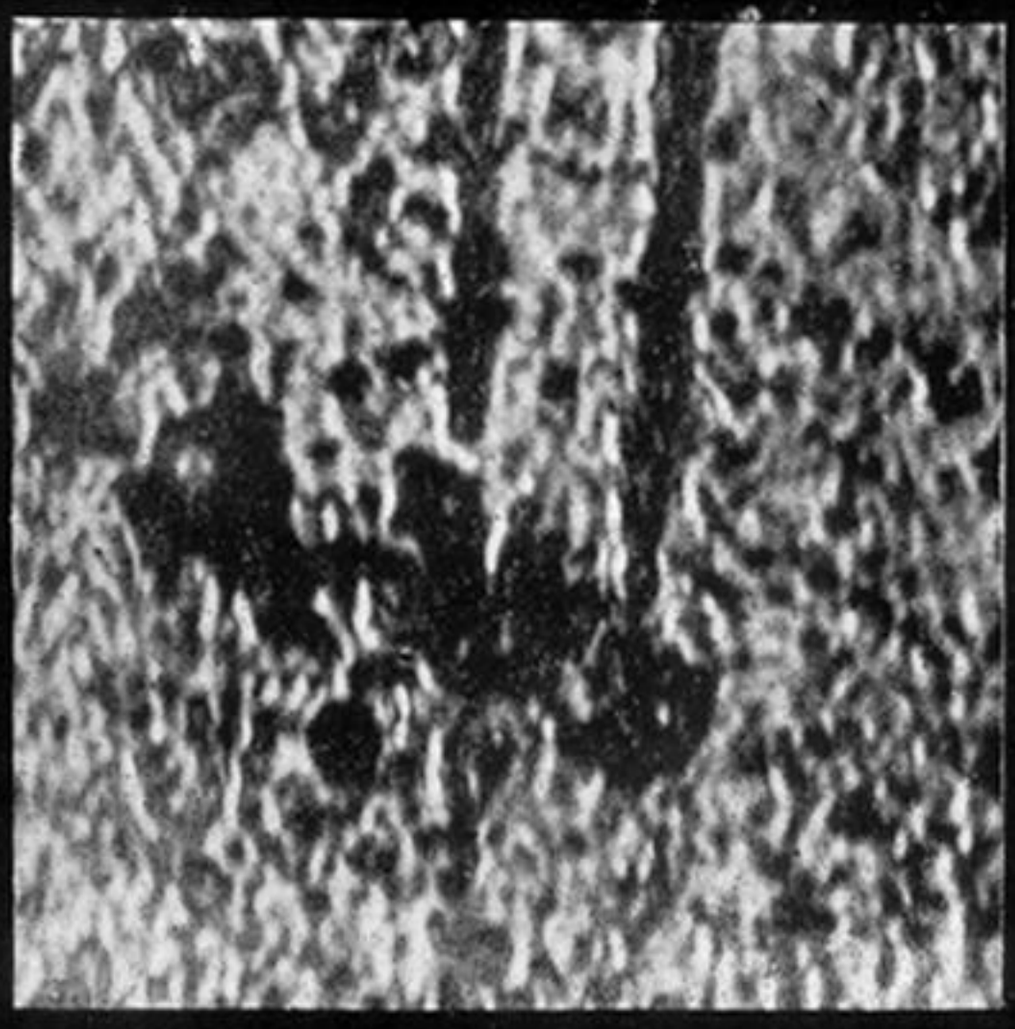

Fig. 21. X1500

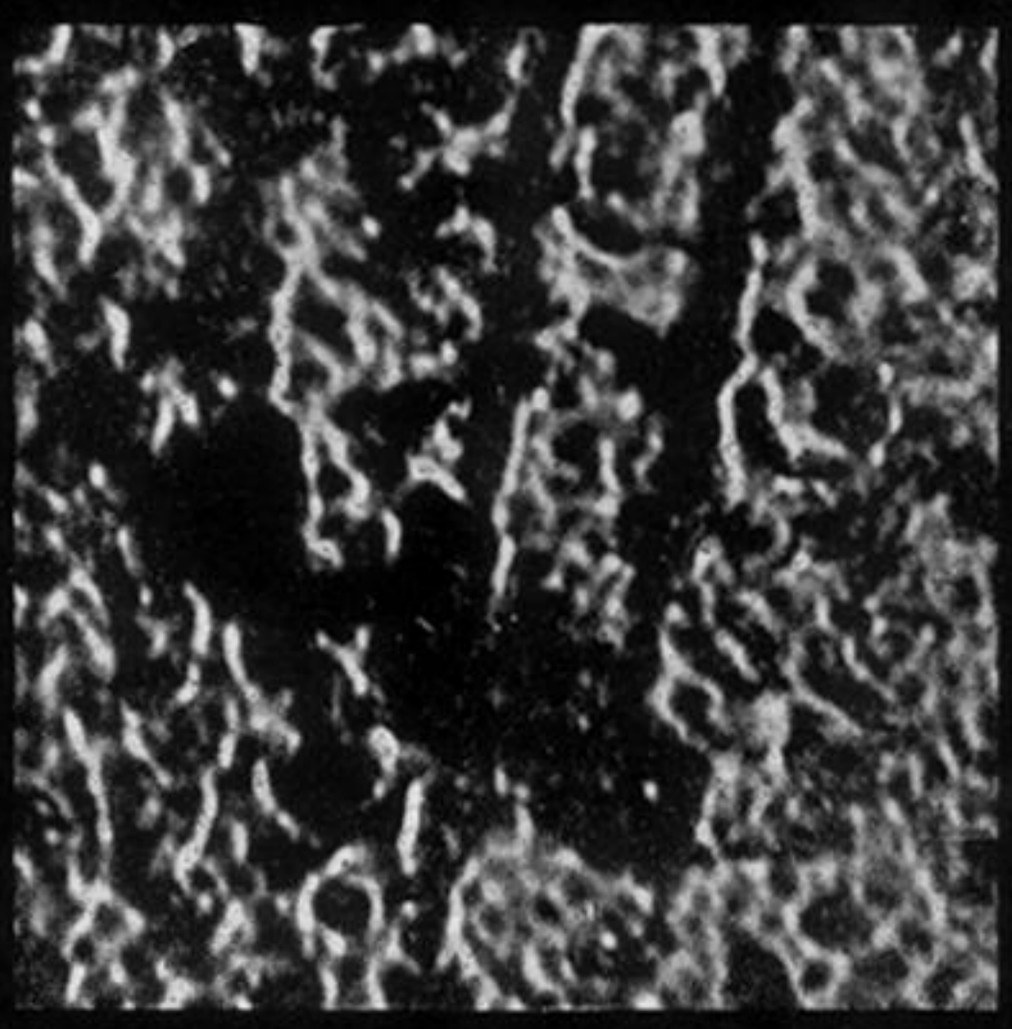

Fig 22 X1500.

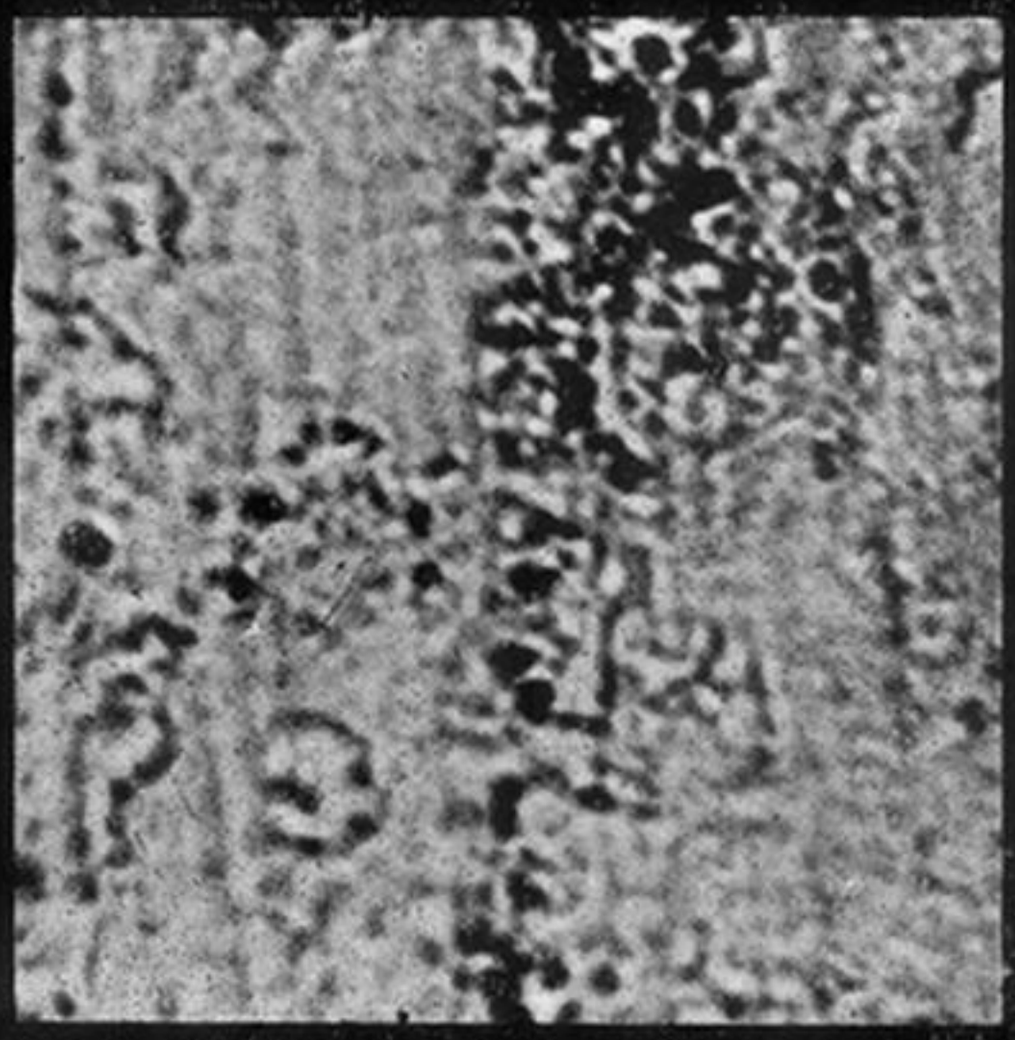

Fig. 23. X1500.

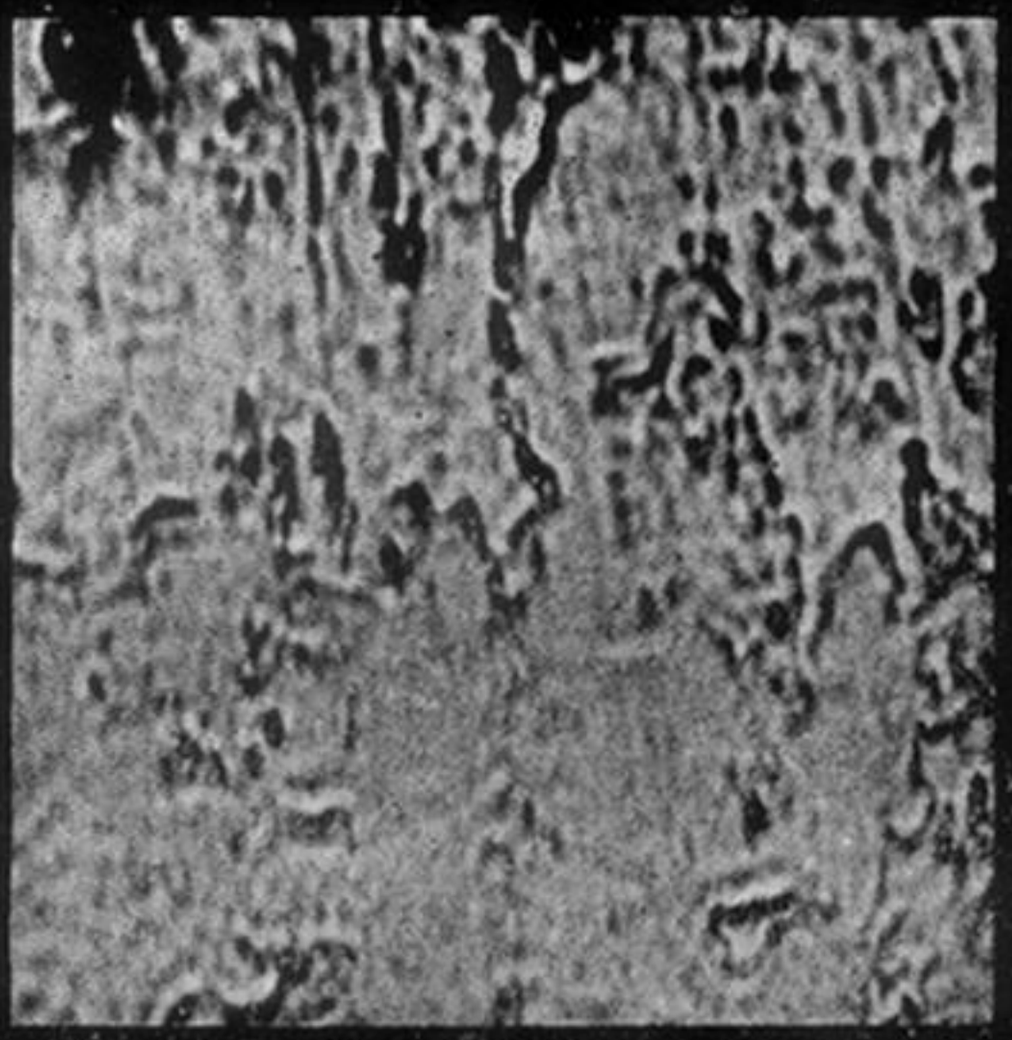

Fig. 24. X1500.

FIG 25. X250.

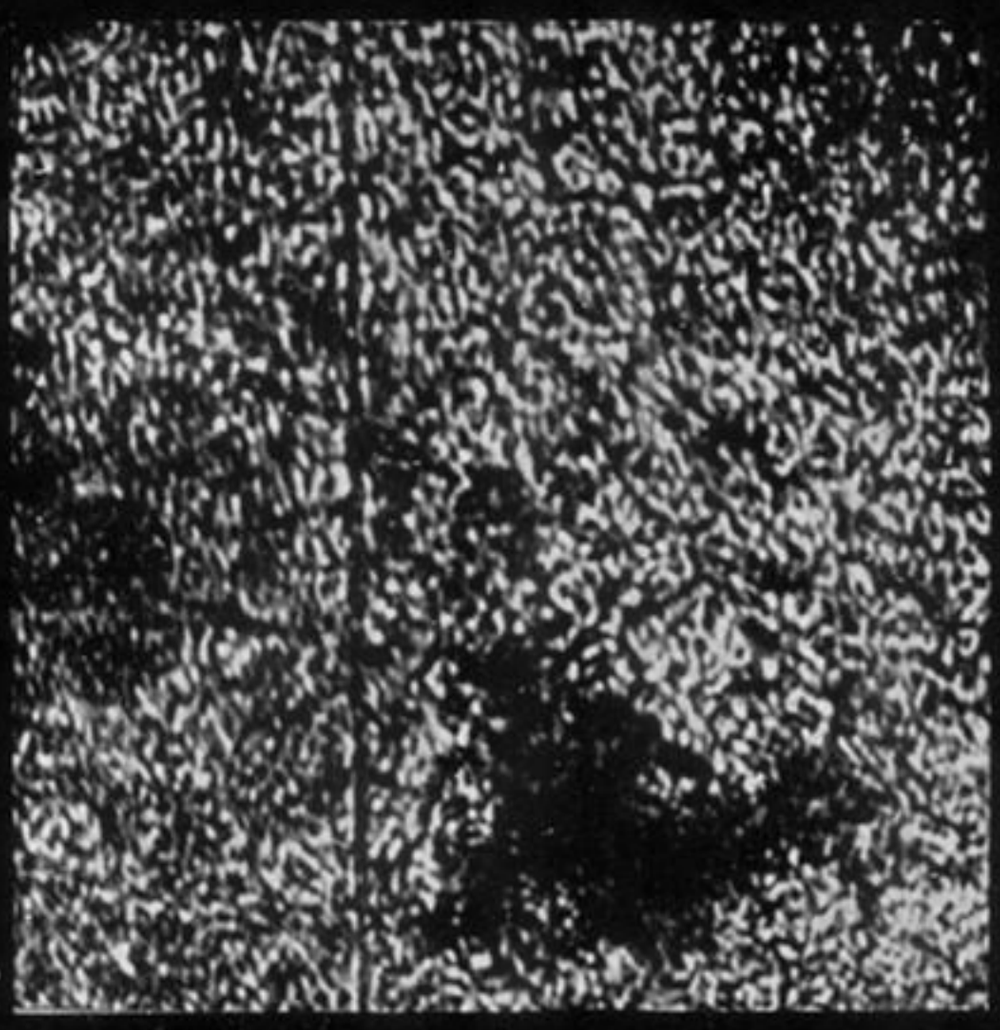

FIG. 26. X775.

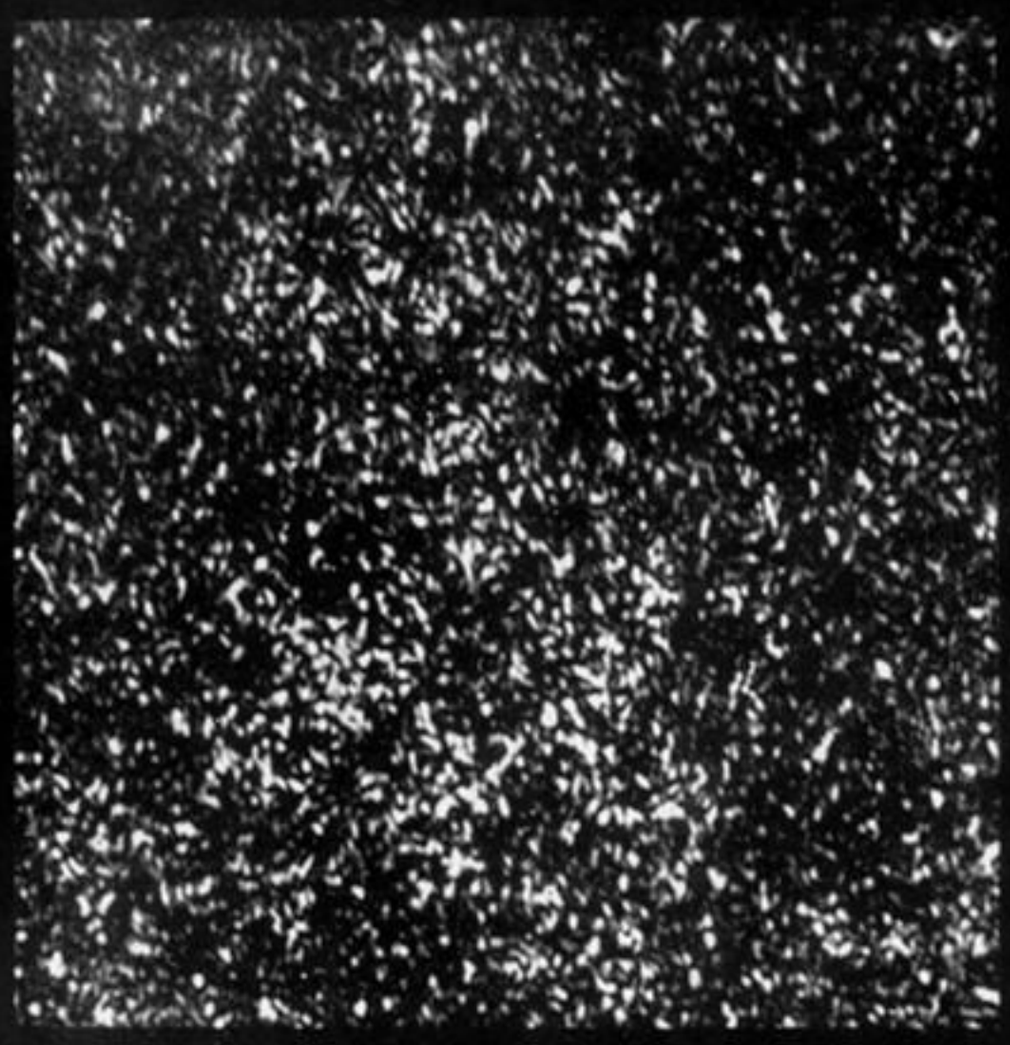

FIG. 27. X 775.

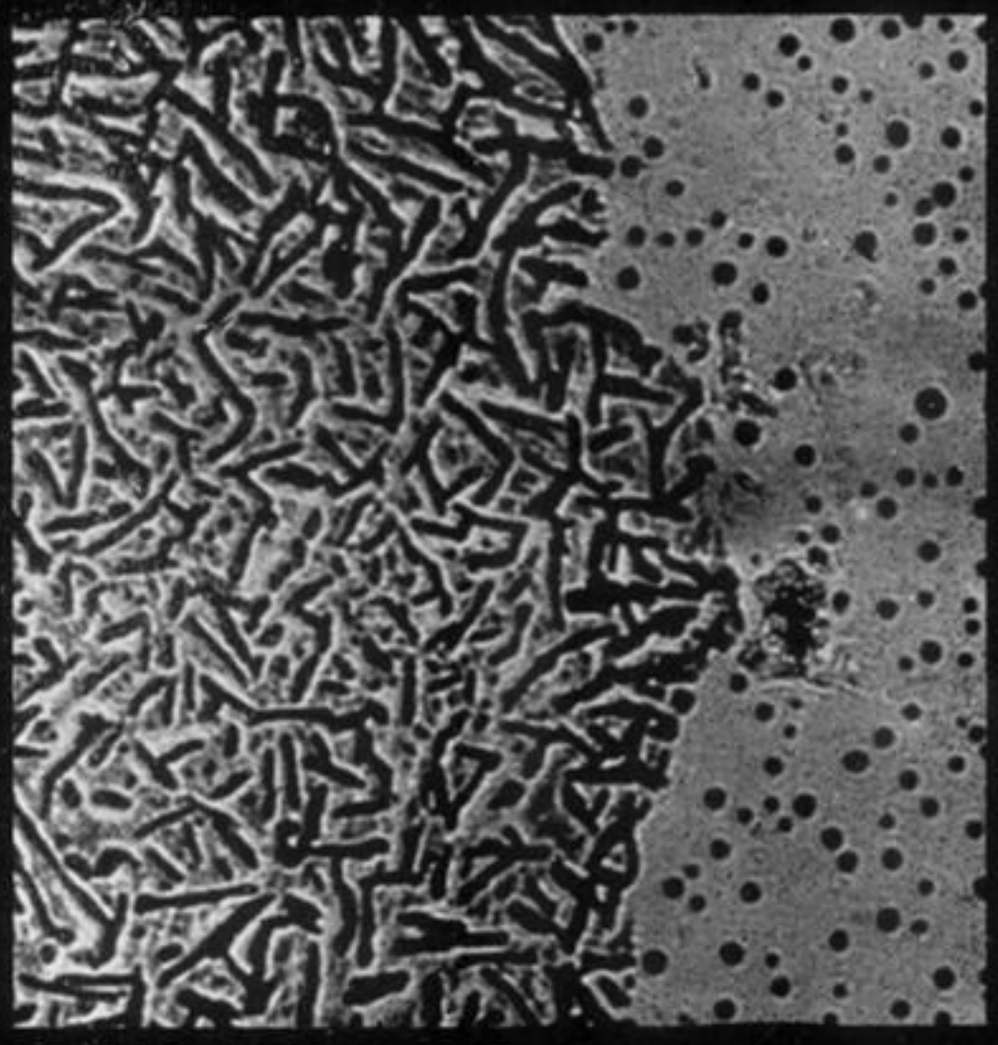

FIG 28. X 440.

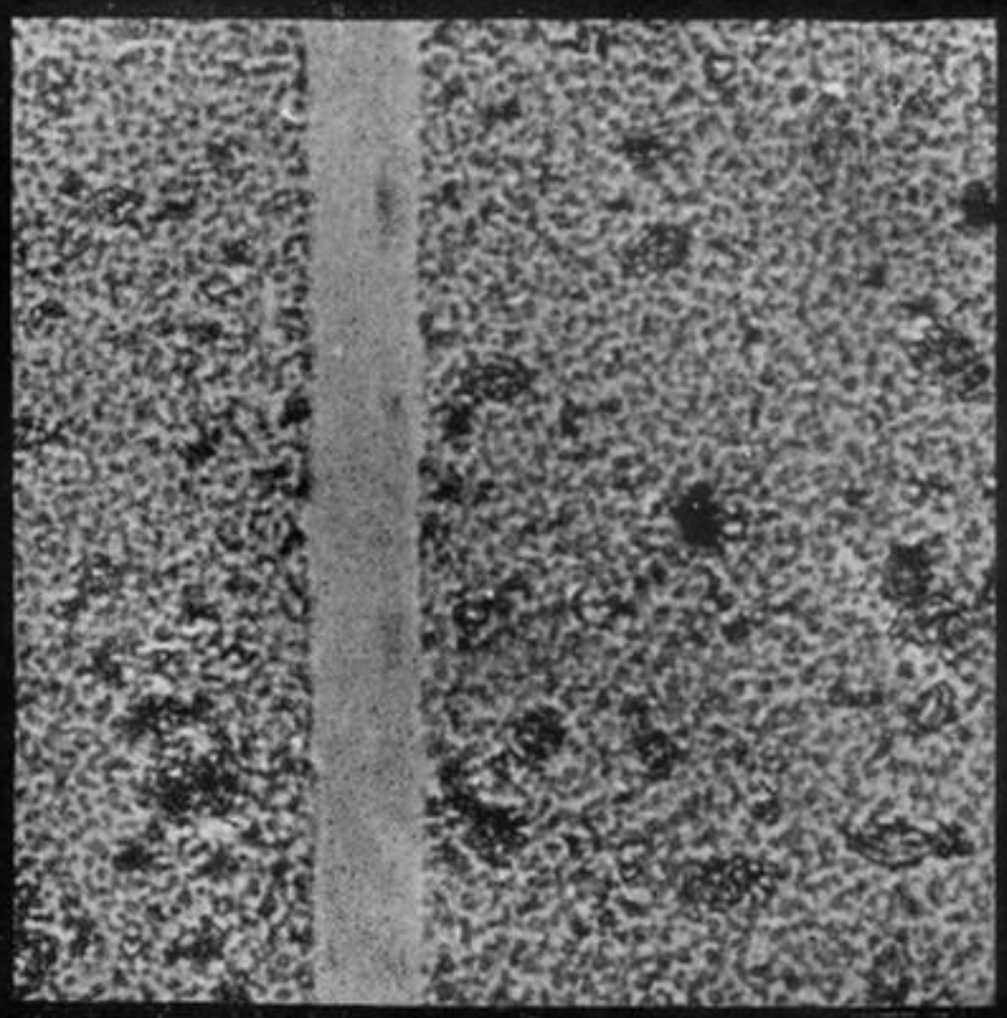

FIG 29. X440

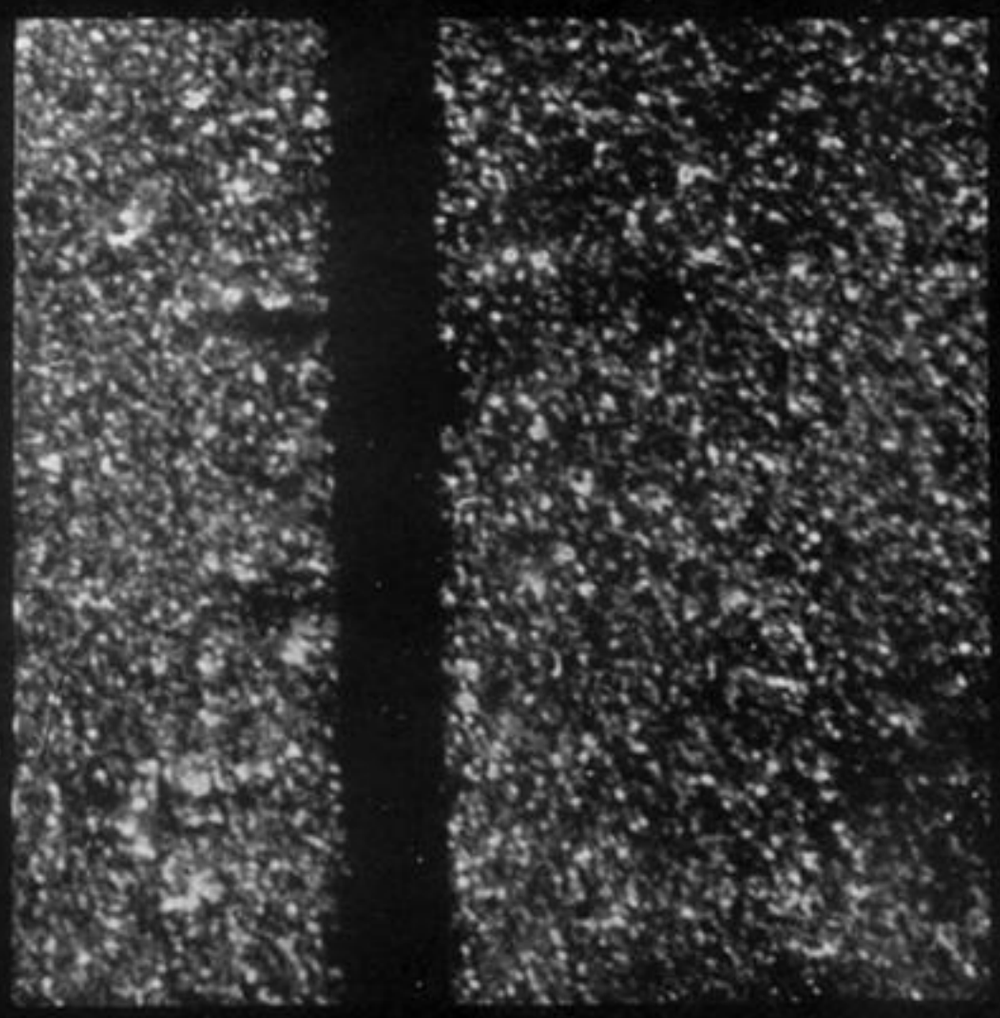

FIG. 30. X440.